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Supporting Information

Correlation of intercalation potential with d-electron configurations for cathode compounds of lithium-ion batteries

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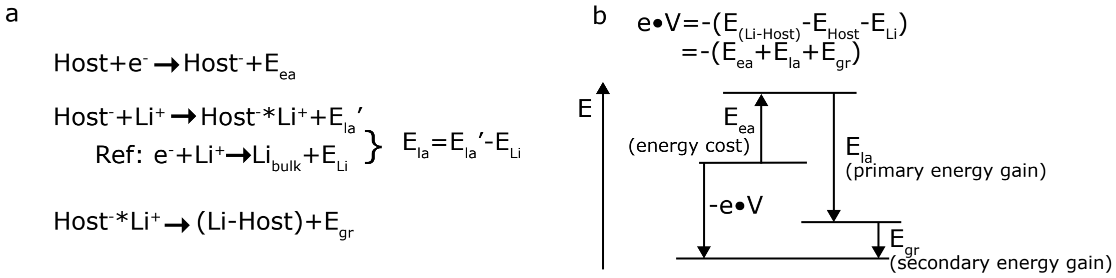

Fig.S1. The three energy terms involved with intercalation potential. (**a**) Equations describing the three decomposed intercalation processes, which define the three energy terms. Host⁻*Li and (Li-Host) represent the intercalated state before and after structure relaxation, respectively. (**b**) Schematic illustration of the relation between the intercalation potential and the three energy terms.

Table S1 The M-O and Li-O bond lengths for layered $LiMO_2$. The units are Å. The "deli" and "li" represent delithiated and lithiated phases, respectively. In the delithiated phase, Li-O bond is measured with Li ions distributed with the fractional coordinates in the lithiated phase. The △d (Li-O) represents the change of Li-O bond length by the Li^+ insertion.

	M-O bond		Li-O bond		
	deli-	Li-	deli-	li-	△d（Li-O)
$LiMnO_2$	1.93	1.95, 2.28	2.04	2.11, 2.17	0.10
$LiFeO_2$	1.96	2.03	2.01	2.12	0.11
$LiCoO_2$	1.88	1.93	2.00	2.07	0.07
$LiNiO_2$	1.86	1.96	1.97	2.08	0.11

Mn^{3+} cation in $LiMnO_2$ is so instable wtihin the initial $R\bar{3}m$ (without Janh-Teller distortion) group that the ligand anions are relaxed to form Jahn-Teller distorted octahedron surround the Mn^{3+} cation forming two kinds of Mn-O bonds with different lengths.

Table S2 The values of energy difference between HS and LS states (E_{HS}-E_{LS}) obtained with first-principles calculations, the parameterized expressions of the term E_{HS}-E_{LS} within CF theory and CF splitting △ estimated from the E_{HS}-E_{LS} term, in the delithiated phases. The units are eV. The label * means the value is hypothetic, not deduced from E_{HS}-E_{LS} term. E.C (HS: LS) represent the d-electron configuration of the cations in HS and LS states.

TME	MO_2				MPO_4				$LiMSiO_4$			
	E.C (HS: LS)	E_{HS}-E_{LS}		△	E.C (HS: LS)	E_{HS}-E_{LS}		△	E.C (HS: LS)	E_{HS}-E_{LS}		△
		value	expression			value	expression			value	expression	
Mn	$t_{2g}^3e_g^0$			2.50*	$t_{2g}^3e_g^1$:$t_{2g}^4e_g^0$	-1.17	$\triangle_O$-$5J_H$	1.33	$e^2t_2^2$:$e^4t_2^0$	-2.97	$2\triangle_t$-$8J_H$	0.52
Fe	$t_{2g}^3e_g^1$:$t_{2g}^4e_g^0$	-0.76	$\triangle_O$-$5J_H$	1.74	$t_{2g}^3e_g^2$:$t_{2g}^5e_g^0$	-1.53	$2\triangle_O$-$10J_H$	1.74	$e^2t_2^3$:$e^4t_2^1$	-1.76	$2\triangle_t$-$10J_H$	1.62
Co	$t_{2g}^3e_g^2$:$t_{2g}^5e_g^0$	0.83	$2\triangle_O$-$10J_H$	2.92	$t_{2g}^4e_g^2$:$t_{2g}^6e_g^0$	-0.61	$2\triangle_O$-$8J_H$	1.70	$e^3t_2^3$:$e^4t_2^2$	-0.69	$\triangle_t$-$5J_H$	1.81
Ni	$t_{2g}^4e_g^2$:$t_{2g}^6e_g^0$	1.03	$2\triangle_O$-$8J_H$	2.52	$t_{2g}^5e_g^2$:$t_{2g}^6e_g^1$	0.24	$\triangle_O$-$4J_H$	1.81	$e^4t_2^3$			0.80*